but twenty-five miles south of Chalk creek had decreased one-half, and the best agates were only in the caps of two inches. The dis-- integration of the sand-rock would of itself give a poor soil. While this is its character in many places, in others we found a mixture of vegetation, which was fertile. Springs and streams are not abund- ant, but where found (like others in sandstone regions), the water is good; and we will add, that in all our experience of eight summers camping in western Kansas, *we have never met with a single " alkali" spring, or a single acre white with alkali deposit.* There are a few, and but a few, salt springs which may at some day be made useful in furnishing settlers with salt.

We have thus given a few notes of this important geological formation, showing how little we yet know of our own territory.

ON DETERMINING THE SOLUBILITIES OF METALLIC SALTS.

BY PROFS. GEO. E. PATRICK* AND ALFRED B. AUBERT.†

The determination of the solubility of a metallic salt in water or other solvent is apparently a matter so simple and so easy of execu- tion as to offer little difficulty to the chemist ; and hence one would naturally expect that the results of different chemists, who have in- vestigated the solubility of the same salt, would show the greatest concordance. But notwithstanding this apparent simplicity, any one who has reviewed the subject must admit that the results obtained by different workers in this field show a lamentable lack of harmony. This lack of harmony must be due to the neglect of certain precau- tions essential to accurate work, which precautions must relate to one or all of the following points:

I. Purity of material.

II. Degree of saturation of the solvent at the temperatures at which the determinations are made.

III. Reliability of the process by which the amount of dissolved salt is estimated, and accuracy in the execution of that process.

Upon the first and third points the liability to error is compara- tively slight, the exercise of ordinary care only being necessary. But upon the second point there is the greatest danger of error; for unless special precautions are taken, it is difficult to obtain a solution at any given temperature, containing the *normal amount* of salt for

*Professor of Chemistry and Physics, Kansas University.
†Professor of Chemistry in Maine Agricultural College.

that temperature, *and no more;* for it is now quite well established that the ability to form *super-saturated* solutions, so strikingly exhibited by sodic sulphate (Glauber's salt), is likewise possessed in some degree by all salts — by most, it is true, in so slight a degree as to be, under ordinary circumstances and for ordinary purposes, quite inappreciable, but in such a degree, however, as to furnish ground for the belief that, unless carefully guarded against, it may, in the determination of solubilities, materially vitiate the results. Indeed, it seems probable that to the phenomenon of super-saturation are due most of the discrepancies so apparent between the different tables of solubilities. In support of this conclusion, we would refer to the manner in which the determinations of solubilities have, as a rule, been conducted.

The plan usually adopted is: to make a saturated solution of the salt at the boiling point of the solvent (or of the saturated solution) and allow it to cool gradually, with frequent or occasional agitation by the hand to prevent super-saturation, to the respective temperatures at which the determinations are made; at which temperatures portions of the liquid are withdrawn, and the amounts of dry salt contained therein determined.

By such a method, where the temperature is being continually lowered, and there are no means of constant agitation, there is evidently a possibility, if not a probability, that super-saturation will occur. It was the object of the work herein described to ascertain if it were not possible, by a simple mechanical contrivance and a different method of work, to avoid the errors arising from this cause; and to that end was employed the apparatus figured below. It consists of a copper tank *A* (shown here in section), inside of which revolves a bottle *B*, containing the salt to be dissolved and the solvent. This bottle is perforated at the base and at the side. Though the perforation at the base, fitted tightly with a rubber stopper, passes a glass tube *c c*, having its outer end closed by a rubber tube and a pinch-clamp *f*. This tube serves as an axis of revolution, the power being applied by means of a cord passing over the grooved wheel *e e*, which is firmly attached to the tube *c c*, just outside the tank. The same tube also furnishes a means of producing pressure in the bottle sufficient to force out the solution through another tube *d d*, passing through a tight stopper in the neck of the bottle, which tube also serves as the axis of revolution. This tube is furnished with a tightly fitting piston *p;* and at a short distance outside the tank it has an orifice *o*, through which, when the piston is drawn out beyond that point, the solution is forced. Within the bottle this

tube is bent so as to allow its end h, to be under the surface of the liquid in the bottle, even when but little remains.
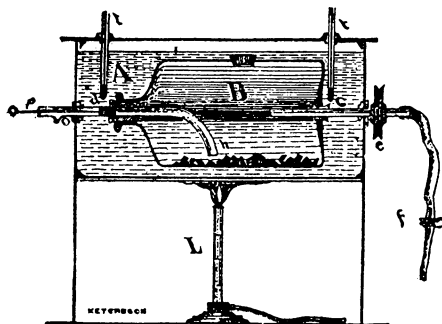
The perforation g at the side, fitted tightly with a stopper, is for the purpose of introducing crystals of the salt as often as necessary, to keep the latter in excess of the solvent.

The lamp L, beneath the tank, serves to regulate the temperature, which is indicated by the two thermometers, $t\,t$.

For maintaining the bottle in revolution, any constant power may of course be used; but in the work already done with this apparatus, the motor employed has been a small electro-magnetic engine, excited by two Bunsen elements.

Our method of work is as follows: A large amount of the salt is introduced into the bottle (the amount depending of course upon the solubility of the salt under examination), the bottle nearly filled with distilled water, and put firmly in place. The tank is filled with water to a level above the top of the bottle, the latter set in revolution by the motor, and the lamp lighted. The temperature of the water in the tank, indicated by two *trusty* thermometers, is slowly raised to the *lowest* temperature at which a determination is to be made, and carefully kept at that point for one-half hour (or longer, if that is found insufficient for obtaining a saturated solution), special care being taken to avoid its getting at all — even a fraction of a degree — *above* the desired point, in order that super-saturation may be absolutely impossible.

At the end of one half-hour (or longer, if necessary) at that temperature, the machine is stopped and allowed to remain quiet ten or fifteen minutes, that the crystals may settle; the tube $d\,d$ being turned at such an angle that the end h is in clear liquid, and not in the vicinity of crystals. A drawing is then made in the following manner: The piston p is drawn out until the opening o is cleared. One person blows into the bottle through the tube $c\,c$ and its rubber attachment, at the same time pressing the clamp f, while another holds

a tarred beaker provided with a ground-glass cover (the beaker itself having a ground edge) under the orifice *o* until the proper amount of solution is obtained. The ground-glass cover is quickly placed on the beaker, the whole is allowed to cool, and is then weighed. The amount of salt dissolved in that amount of solution is then determined by the most reliable and convenient method.

Parallel determinations were always made, the second drawing being made about one quarter-hour after the first, the bottle meantime having been kept in revolution, and the temperature constant. The determinations were made usually at intervals of 10° C., ranging from 0° or 10° to 90° or 100°.

In this way the solubilities of salts have been determined, both singly (one salt alone in water), and mixed (two salts, both present in excess of the solvent), with uniformly gratifying results, the curves being in each case more regular than any previously obtained; and all the results, with very few exceptions, show upon comparison with those on record, obtained by the old method of work, smaller amounts of salt dissolved at the respective temperatures — a fact which goes far to prove that super-saturation has, in some cases at least, been a vitiating element in the work.

We give below the curve for the solubility of anhydrous cupric sulphate ($CuSO_4$,) based upon the figures obtained by us, representing the number of parts of the anhydrous salt soluble in one hundred parts of water. We also give for comparison the figures actually obtained for the same salt, showing the magnitude of the discrepancies between parallel determinations.
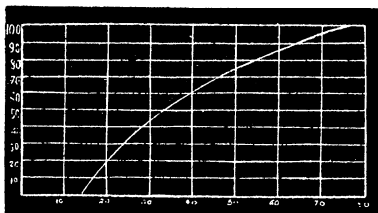
We should state, however, that in this curve the figures for 0° and 100° were obtained with the utmost care by our method of work (raising the temperature, not lowering it), but *not* with aid of the apparatus — flasks having been used instead. This work was performed at the laboratory of Cornell University, and we owe many thanks to Prof. C. H. Wing, non-resident Professor of Chemistry at Cornell, for his kind and valuable suggestions regarding it.

Parts $CuSO_4$ (anhyd.) soluble in 100 parts water.

At 0° C	13.98	14.31	dif.. .33		
At 10° C	17.34	17.65	" .31		
At 20° C	20.58	20.49	" .09		
At 30° C	24.37	24.32	" .05		
At 40° C	28.50	28.50	" .00		
At 50° C	33.34	33.32	" .02		
At 60° C	39.00	39.02	dif., .02		
At 70° C	45.61	45.87	" .26		
At 80° C	54.63	54.33	" .30		
At 90° C	63.50	64.14	" .64		
At 100° C	75.18	75.26	" .08		